

# PATENT SPECIFICATION

Inventors: ARTHUR COLIN BASKET, GEORGE ARTHUR ROOKE  
MATTHEWS and HUGH JAMES SPENCER-PALMER

733.624

Date of filing Complete Specification (under Section 3(3) of the Patents Act, 1949): March 20, 1953.

Application Date: April 10, 1952.

No. 9207/52.

Application Date: April 10, 1952.

No. 9208/52.

Application Date: June 27, 1952.

No. 16214/52.

Application Date: Nov. 13, 1952.

No. 28605/52.

Application Date: Nov. 13, 1952.

No. 28606/52.

Complete Specification Published: July 13, 1955.

Index at acceptance:—Class 2(5), R23(P: T2), R27(P: T2).

## COMPLETE SPECIFICATION

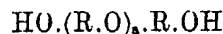
### New Synthetic Resins Derived from Linear Aliphatic Polyethers and Bifunctional Isocyanates and Rubber-Like Materials derived therefrom

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new synthetic resins and their conversion into rubber-like materials.

By the term rubber-like as used throughout this specification we mean having physical properties similar to those of vulcanised natural rubber.

According to the present invention we provide a process for the production of a synthetic resin which comprises reacting under substantially anhydrous conditions an excess of one or more bifunctional isocyanates with one or more linear polyethers having the formula



in which the various embodiments of R are divalent aliphatic hydrocarbon radicals and may be same or different and  $n$  is an integer the average value of which is such that the average molecular weight of the polyether is greater than 1,000. We have found that a rubber-like material having an excellent combination of high tensile strength, high tear resistance, and resistance to abrasion may be produced by heating said synthetic resin in the presence of a basic catalyst or by first modifying the synthetic resin of our invention

with water, steam, ammonia or a compound having two groups each reactable with the isocyanate group, and thereafter subjecting the reaction product to an elevated temperature. Also such rubber-like materials may be obtained by subjecting a composition comprising a synthetic resin according to our invention, and a compound having at least three hydroxyl groups, to an elevated temperature.

Bifunctional isocyanates which may be used are, for example, hexamethylene diisocyanate; 2-nitrodiphenylene-4,4'-diisocyanate; 2-nitrodiphenyl-methane-4,4'-diisocyanate; naphthylene-1,4-diisocyanate; naphthylene-1,5-diisocyanate; naphthylene-2,7-diisocyanate; fluorene-2,7-diisocyanate; chrysene-2,8-diisocyanate; 1-chlorophenylene-2,4-diisocyanate; tolylene 2,4-diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; di-paraxylylmethane-4,4'-diisocyanate; diphenylene-4,4'-diisocyanate and 4,4'-cyclohexylphenyl diisocyanate. Mixtures of any of these compounds may be used.

We prefer to use polyethers which have low melting points and for this reason we prefer to use polyethers in which the consecutive oxygen atoms in the polyether are separated by chains of not more than four carbon atoms, such for example as are obtained by the polymerisation or copolymerisation of the following compounds:— ethylene oxide, isopropylene oxide, trimethylene oxide,  $\alpha$ -methyl trimethylene oxide, 3,3'-dimethyl trimethylene oxide, tetrahydrofurane, 1,3 dioxane and dioxolane. Of these com-

pounds we further prefer to use those which have no side groups since we find that synthetic rubbers derived from such compounds have the best combination of physical properties. Such polyethers may be prepared by any suitable known method, for example, ethylene oxide may be polymerised by the action of water, glycol, acetic anhydride or caustic soda. Tetrahydrofuran may be polymerised by the action of catalytic amounts of fluorosulphonic acid, or boron trifluoride with small amounts of ethylene oxide or propylene oxide, followed by treatment with water. 1,3 dioxane may be polymerised by refluxing under nitrogen in the presence of boron trifluoride acetyl chloride and acetic acid.

Depending upon the method of preparation the polyether may have terminal groups which are not hydroxyl groups, and in such circumstances the non-reactable terminal groups should be replaced by hydroxyl groups by known methods. For example, polyethers having terminal chloro groups may be treated by heating with dilute alkali to replace the chloro groups by hydroxyl groups.

#### Reaction between the Polyether and Bifunctional isocyanate.

In carrying out the process of our invention the polyether is reacted with the bifunctional diisocyanate preferably at an elevated temperature, for example 120°—160° C. This enables the reaction to be completed rapidly. The reaction must be carried out under substantially anhydrous conditions, that is to say, water must be excluded to a sufficient extent that the reaction proceeds essentially between the polyether hydroxyl groups and the isocyanate groups. We have found that the reaction proceeds satisfactorily provided the water content of the reaction mixture does not exceed about 0.1% of the weight of the reaction mixture.

It is also preferable that the polyether should be free from acid since the presence of acid may have an inhibiting effect upon the reaction between the bifunctional isocyanate and the polyether. The mixture of bifunctional isocyanate and polyether should therefore be neutral or slightly alkaline, e.g., an acid polyether can be made alkaline by the addition of a basic material. The basic material is preferably one that does not react with any of the other ingredients and has a relatively low boiling point, e.g. less than 100° C. so that excess can be removed easily. Suitable basic materials are organic tertiary bases, e.g. triethylamine. A considerable part of any residual acidity from the pre-

paration of the polyether can be removed by boiling with water, e.g. down to an acid number of 4 or less and only the final traces need be removed by the basic material.

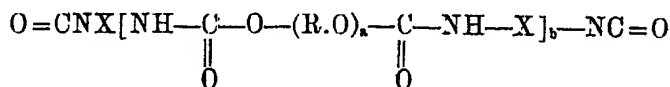
The polyether is most conveniently dried before carrying out the reaction by heating, e.g. at 120° C. in the liquid state in a current of a dry inert gas, e.g. nitrogen or carbon dioxide, and, if desired, under reduced pressure. It will be appreciated that in reacting the polyether with the bifunctional isocyanate there may be some cross linking although the final product is essentially a linear compound. Where there is no cross linking the synthetic resin is normally a sticky semi-solid material, but where there is a slight degree of cross linking the compound tends to be more rubbery.

It is necessary that an excess of bifunctional isocyanate over the polyether should be used in order to produce a synthetic resin having terminal isocyanate groups. The relative amount of bifunctional isocyanate chosen will determine to what extent chain lengthening of the polyether molecules is allowed to proceed. Thus, when the amount of bifunctional isocyanate is only slightly more than one mole per mole of polyether, there will be a considerable degree of chain lengthening. When the amount of bifunctional isocyanate is greater than two moles per mole of polyether there will be substantially no chain lengthening of the polyether. The physical properties of our product and its rubber-like derivative are controlled by the ratio of the reactants, by their molecular weights and their structures. It is necessary therefore to vary the amount of bifunctional isocyanate which is used according to the molecular weight of the polyether.

We prefer that the polyethers used in our invention should have average molecular weights greater than 1,400 in order to obtain good quality rubber-like products and achieve economy in raw materials, and that for the former reason the synthetic resin of our invention should have an average molecular weight greater than 5,000. Too high a molecular weight in the polyether should be avoided since as the molecular weight is increased the degree of cross-linking in the final rubber-like product is reduced. Also, with very high molecular weight polyethers, there may be increased tendency to crystallise which may affect the physical properties of the rubber-like material produced therefrom, e.g. there may be a tendency to cold-harden or to stretch embrittlement.

With polyethers having an average

molecular weight below 5,000 it is desirable therefore that there should be some chain lengthening during the treatment with the bifunctional isocyanate, and for such polyethers particularly useful amounts of bifunctional isocyanate are from 1.2 to 2 moles per mole of polyether. With polyethers having average molecular weights below 5,000 the amount of bifunctional isocyanate which is used may be varied within these limits according as to whether the synthetic resin is to be pressed in a heated mould into a rubber-like product or cast into sheet form as hereinafter described. Where our resin is to be moulded a suitable resin is obtained by using low concentrations of the bifunctional isocyanate within these limits, and where our resin is to be cast, higher concentrations of the bifunctional isocyanate should be used since these give a more fluid product. With polyethers having an average molecular weight above 5,000 and particularly above 7,000 we prefer that there should be no substantial degree of chain lengthening. Although theoretically this can be achieved by using 2 moles of bifunctional isocyanate per mole of polyether, we prefer to use an excess of up to

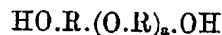


in which the various embodiments of R are divalent aliphatic hydrocarbon radicals and may be the same or different, the various embodiments of X are divalent organic radicals and may be the same or different, a and b are integers and the average value of a is such that the average molecular weight of  $HO(R.O)_aH$  is greater than 1,000. The average value of b is preferably such that the synthetic resin has an average molecular weight of at least 2,000. If there has been chain-lengthening during the modification of the polyether with the bifunctional isocyanate, as is desirable when the average molecular weight of the polyether is below 5,000, the value of b will be two or more in the majority of the molecules of the synthetic resin. If there has been no chain-lengthening, as is desirable when the average molecular weight of the polyether is above 5,000, the value of b will be one in the majority of the molecules of the synthetic resin. In producing a rubber-like material, our synthetic resin is cross-linked by one of the various methods described herein. The product thus obtained is a rubber-like material comprising polyether chains chemically linked together by residues of at least one bi-

30 functional isocyanate. The production of our synthetic resins from polyethers having an average molecular weight greater than 5,000 is advantageous economically, since the amount of bifunctional isocyanate, which is normally the more expensive reactant, needed to produce a synthetic linear resin of a given molecular weight, is less than needed to produce the same molecular weight synthetic resin from a relatively low molecular weight polyether.

The molecular weights of polyethers referred to throughout this specification and in the appended claims are average molecular weights and were determined by ebulliometry. Molecular weights of the synthetic resins of our invention, when referred to, are theoretical molecular weights based on the assumption that they are linear synthetic resins and no cross-linking reactions occur in their preparation.

The synthetic resin of our invention, in its linear form comprises polyether chains having terminal isocyanate groups and may be represented by the formula:—



functional isocyanate and/or derivatives thereof, wherein the polyether chains each have the formula  $-R.(O.R)_a-$  in which the various embodiments of R are divalent aliphatic hydrocarbon radicals and may be the same or different and a is an integer the average value of which is such that the average molecular weight of

is at least 1,000. The final step of the process may comprise either a casting process in which the material to be cast is heated in an open mould to form a rubber-like sheet, or a moulding process in which the material to be moulded is subjected to heat and pressure to form a moulded article. We prefer that when a casting process is used that our synthetic resin, whether reacted or mixed with other compounds as described herein, or not, should be in a substantially linear condition with or without chemical modification as described hereinafter, since the casting process is thereby facilitated. When, on the other hand the final step is a moulding process in which pressure is used, we prefer that the material which is fed into

the mould should be modified by some degree of cross-linking by a heat and/or masticating treatment with or without a modifying reagent as described herein-  
 5 after, since this is a convenient form to handle for moulding purposes; the material should of necessity be cross-linked only to the extent that it is still capable of being moulded and this stage  
 10 is normally reached when the material is in the form of a crepe which is capable of being worked on heated rolls.

Conversion of the synthetic resin to a rubber-like material by heating in the presence of a catalyst.

The synthetic resin of our invention may be converted into a synthetic rubber by heating in the presence of a basic catalyst. The catalyst may be organic or  
 20 inorganic and is preferably one which does not contain groups which react with isocyanate groups. Examples of catalysts are: alkoxides, e.g. sodium methoxide, sodium ethoxide; inorganic bases, e.g.  
 25 calcium oxide or hydroxide, barium oxide or hydroxide, beryllium hydroxide, lithium hydroxide and sodium hydroxide; and tertiary organic bases, e.g. trimethylamine, triethylamine, tripropylamine,  
 30 tributylamine, triamylamine, tribenzylamine and dimethylaniline. The amount of catalyst required is normally within the range 0.05 to 0.5% based on the weight of the synthetic resin. When the  
 35 synthetic resin has been prepared from the less reactive diisocyanates, e.g. aliphatic diisocyanates, the more reactive catalysts such as the alkali hydroxides are best used to increase the speed of the reaction.  
 40

The catalyst can be incorporated into the polyether before reacting with the bifunctional isocyanate or it may be added to the synthetic resin of our invention.  
 45 The properties of the final product will depend upon the uniformity of the reaction which proceeds when the synthetic resin is heated in the presence of the catalyst. It is therefore important that  
 50 the catalyst should be uniformly dispersed throughout our resin. When the synthetic resin is sufficiently fluid the catalyst may be dispersed efficiently in a stirred mixer. It is more usually necessary at this stage  
 55 to masticate the catalyst into the resin on a mill or in a Banbury type mixer. Other auxiliary ingredients, e.g. colouring materials, may be incorporated. The synthetic resin at this stage is slightly cross-linked and is usually in the form of a rubbery crepe. It may be converted into a fully cross-linked synthetic rubber as hereinafter described.

Treatment of the synthetic resins with a bifunctional reactable compound.

As in the case with dispersions of catalysts for the production of rubber-like materials by catalytic action an important feature in controlling the properties of our rubber-like product when an intermediate modified resin is produced, is the control of the uniformity of the reaction between the synthetic resins of our invention and the modifying reagent. Where the reaction mixture is sufficiently fluid the reaction may be carried out solely in a stirred mixer. In other cases the initial stage of the reaction may be carried out in a stirred mixer but as the reaction proceeds the nature of the product changes and in order to keep the product effectively mixed so that the reaction can proceed to the desired extent, the final stage of the mixing should preferably be carried out on heated rolls or in a mixer of the Banbury type. The temperature at which this reaction is allowed to proceed will depend upon the type of compound with which the synthetic resin of our invention is reacted. When water is used the reaction can be carried out below 100° C., e.g. at 80° C., but we prefer to use higher temperatures of the order of 120—160° C. and when the material is further reacted under masticating conditions we prefer this further reaction to be at 103°—140° C. The reaction with steam is similarly preferably carried out at temperatures from 120—160° C. followed, if desired, by mastication at, for example, 103°—140° C. With diamines, dicarboxylic acids and amino acids on the other hand, it is preferred that the synthetic resin should be cooled before the reaction is allowed to begin in order to allow thorough mixing of the ingredients before further reaction at the higher temperatures.

The synthetic resin may be modified by adding the reactant, e.g. water, in a suitable mixing vessel, or mastication, or in the case of steam and ammonia it may be blown on to the surface of the product.

Compounds having two groups each reactable with the isocyanate group and which may be reacted with the synthetic resin of our invention include, glycols, diamines having primary or secondary amino groups, dicarboxylic acids, hydroxy amines, hydroxy acids and amino acids. Suitable compounds are, for example, ethylene glycol, 1:3 propane diol, 1:4 butane diol, ethylene diamine, trimethylene diamine, tetramethylene diamine, m-phenylene diamine, naphthylene diamines, tolylene 2,4 diamine, aminobenzyl aniline, amino-diphenyl-

amine, 2-amino ethyl alcohol, 2-amino 1 naphthol, m-aminophenol, glycollic acid, α-hydroxy-propionic acid, amino acetic acid and amino benzoic acid. The bifunctional compound used should preferably have a relatively low melting point, e.g. below 150° C. for ease of mixing.

The choice of compounds best suited for modifying our synthetic resins prior to vulcanisation depends upon the reactivity of the isocyanates used in the preparation of the resins. Thus, if the relatively unreactive aliphatic isocyanates are used, the modifying reagent should be a compound resulting in the formation of reactive groups, e.g. water, ammonia, an amino or carboxylic acid in order that the vulcanisation should be reasonably rapid, or if one of the less reactive modifying reagents is to be used, e.g. 1,4-butane diol, it is best used in conjunction with a basic catalyst. On the other hand, the tendency to reaction between the synthetic resin and the modifying reagent should not be so great that the rapid vulcanisation which results prevents their intimate admixing. Thus, when an aromatic diisocyanate is used in the production of the synthetic resin, a reactive modifying reagent, such as an aliphatic diamine, is normally not suitable and, if an aromatic diamine is used as modifying reagent for such a resin, it should be one having hindering groups in the nucleus, e.g. 3,3' dichlorobenzidine, if ease and uniformity of mixing is to be effected.

The physical properties of the rubber-like product which may be obtained depends upon the nature of the synthetic resin of our invention and the nature and particularly the amount of the reactant with which it is reacted, for which only an amount of reactant sufficient to bring about poly-addition between a proportion of the terminal isocyanate groups is required. Excess of the reactant should be avoided because it has a degrading effect on the physical properties of our final cured rubber-like material. The amount of reactant used is, in fact, best judged by observing the change in a physical property of the rubber-like product. When the reactant to be used is not volatile at the reaction conditions, and the amount required has been determined by trial, it may then be added to the synthetic resin of our invention in weighed amount. In the case of water, the water may be added in the form of a hydrated salt, e.g. as sodium sulphate decahydrate. When losses of the reactant occur, e.g. because of volatility in the case of steam, special process control to ensure correct addition is required. Interreaction be-

tween the reactant molecules, e.g. in the case of glycols, may also make special process control necessary. When water is used the amount is normally between 0.4 and 1.5% by weight of the material being treated.

Rubber-like materials and intermediates for their production.

Our synthetic resin whether containing a catalyst or whether reacted with bifunctional compound, is normally moulded as a crepe or cast into a form required. It may, however, also be converted into the form of ribbon, film, sheets, fibres, filaments and, solutions or dispersions for coating and impregnation. The production of a moulded rubber-like material is best achieved by heating the partially cross-linked crepe to an elevated temperature of, for example, 140—170° C. for a period of, for example, 10—30 minutes if necessary at a pressure of the order of 0.5 to 1 ton/square inch. The casting process may be carried out by pouring the synthetic resin containing a catalyst or the synthetic resin after reaction with a bifunctional compound, preferably in the substantially linear condition, and if necessary at an elevated temperature, into an open mould and heating without pressure. Also, where our synthetic resin has been reacted with a compound, e.g. water or steam, which gives rise to the evolution of a gas during the reaction, an expanded rubber-like material may be obtained by heating the reaction product in a suitable mould. The formation of the rubber-like material may be speeded up or carried out at a lower temperature by incorporating into the product obtained by reacting our synthetic resin with a bifunctional compound a suitable catalyst, e.g. an inorganic or an organic basic compound as hereinbefore described. When the bifunctional compound used is a diamine or contains an amino group, the use of such a catalyst is not normally necessary.

At any stage before the final heating step, ancillary ingredients such as, for example, fillers, plasticisers, extenders, pigments, or other materials may be incorporated in the material.

Preparation of a composition comprising the synthetic resin and a polyhydroxy compound and its conversion to a rubber-like material.

Compositions comprising a polyhydroxy compound and the synthetic resin of our invention are prepared by mixing the required amount of the poly-

hydroxy compound into the synthetic resin until a homogeneous product is obtained. Any polyhydroxy compound having three or more primary and/or secondary alcohol groups are suitable though compounds with melting points less than 150° C. are preferred as they are mixed with the resins easily. Examples of such compounds are glycerol, pentaerythritol, trihydroxy tertiary butane, trimethylol propane, trimethylol ethane and 1,2,4 butane triol or Novolak resins of low molecular weight. Mixtures of such compounds may be used.

For ease of working it is usually found convenient to mix the polyhydroxy compound into the hot synthetic resin immediately after it has been prepared. Where, however, it is not intended to convert our composition into a rubber-like material immediately after its preparation it should be cooled to room temperature or below. The relative amounts of the polyhydroxy compound and the synthetic resin are preferably such that the hydroxyl groups and terminal isocyanate groups are present in substantially equivalent amounts. The amount of polyhydroxy compound required for this purpose will therefore depend upon the molecular weight of the linear synthetic resin. We prefer to avoid an excess of hydroxyl groups over the isocyanate groups because such hydroxyl groups take no part in the cross-linking process and are therefore redundant. There is no such objection to the presence of a small excess of isocyanate groups.

The composition of our invention is preferably used for moulding purposes within a comparatively short time of its preparation. The reaction between the polyhydroxy compound and the synthetic resin can be retarded to a certain extent by cooling to a low temperature, but the composition should preferably be kept not more than a few hours before being subjected to the moulding operation.

Our composition is normally moulded as a crepe or cast into a form required. It may, however, also be converted into the form of ribbon, film, sheets, fibres, filaments, and solutions or dispersions, for coatings and impregnation. Our composition may be moulded or cast by the methods described hereinbefore.

At any stage before the final heating step, ancillary ingredients such as, for example, fillers, plasticisers, extenders, pigments or other materials, may be incorporated in the material.

Our invention is illustrated but not limited by the following examples in which the parts are given by weight.

#### EXAMPLE I.

200 parts of tetrahydrofurane maintained at 0–10° C., were mixed with 10 parts of fluorosulphonic acid. The mixture was maintained at about 20° C. for two-days and was then boiled with water. The top layer was removed and boiled with successive amounts of water to remove the catalyst, until the acid number was reduced to 4 or less, that is to say, the residual acidity was equivalent to less than 4 milligrams of potassium hydroxide per gram of polymer. Sufficient triethylamine was then added to remove the remaining acidity and the polymer was dried by azeotropic distillation with benzene, the residual benzene being distilled off. The polymer was dried by blowing dry nitrogen through it at 120° C. The polyether so obtained had an average molecular weight of 2,000.

100 parts of the dry polyether were mixed with 15 parts of hexamethylene diisocyanate at 140° C. in a heated Bridge mixer for a period of 30 minutes. The reaction product was cooled and the somewhat rubbery product was broken up. 50 parts of this product were placed in a cold positive mould and moistened with 1½ parts of water. The mould was heated to 160° C. and closed under a pressure of 0.5 tons/square inch for 30 minutes. The moulded material in the form of a disc was removed from the mould and was found to be highly transparent and to have a tensile strength of 1,400 lb./square inch and an extension at break of 700%.

#### EXAMPLE II.

Tetrahydrofurane was polymerised in a manner similar to that described in Example I but using 6 parts of catalyst, and the polyether so obtained had a molecular weight of 1,600. 100 parts of the dry polyether were mixed with 12.5 parts of tolylenediisocyanate in a Bridge mixer heated to 140° C. for a period of 30 minutes. 0.35 parts of tolylene diamine were added and after 40 minutes further mixing the reaction product was transferred to a two roll mill, the rolls of which were maintained at 103° C. and 110° C. respectively to form a uniform crepe. The product was then moulded into the form of a disc in a mould heated to 140° C. under a pressure of 0.5 tons/square inch for 15 minutes. A tough rubbery material was obtained.

#### EXAMPLE III.

200 parts of tetrahydrofurane were polymerised by the method described in Example I except that 15 parts of fluoro-



5 sulphonic acid were used. The polyether so obtained had a molecular weight of 1,400. 100 parts of the dry polyether were mixed with 15 parts of tolylene diisocyanate at 140° C. for 30 minutes.

10 (a) 20 parts of the product were mixed with 0.1 parts of triethylamine at 140° C. and the mixture was quickly poured into a flat mould so that it formed a thin layer in the mould. The mould was then maintained at 110° C. for 16 hours. The product was stripped from the mould and was a pale brown transparent tough rubber.

15 (b) A second 20 parts of the product were mixed with 0.26 parts of 1:4 butane diol. The mixture was heated to 140° C. and poured into a flat mould which was then heated at 110° C. for 16 hours. At the end of this time the product was stripped from the mould and it was a pale brown transparent tough rubber.

#### EXAMPLE IV.

25 200 parts of tetrahydrofurane were polymerised by the method described in Example I except that 8 parts of fluoro-sulphonic acid were used as catalyst. The polyether so obtained had a molecular weight of 3,200. 50 parts of the dry polyether were mixed with 4.75 parts of naphthalene 1,5 diisocyanate at 150° C. in a Bridge mixer for 5 minutes. 0.1 parts of sodium methoxide were added and the mixing was continued for 30 minutes. The product was placed in a mould heated to 140° C. and subjected to a pressure of 0.5 tons/square inch for 20 minutes. After removal from the mould the moulded sheet was heated at 80° C. for 16 hours. The product was a tough abrasion resistant rubber having a tensile strength of 4,000 lb./square inch, an extension at break of 720% and a tear resistance of 680 lb./square inch.

#### EXAMPLE V.

45 200 parts of tetrahydrofurane were polymerised exactly as in Example 4 and 100 parts of the product were reacted with 9.5 parts of naphthalene 1,5 diisocyanate at 150° C. in a stirred mixer for 5 minutes. At the end of this time 0.5 parts of tri-n-amylamine were added. The mixture was immediately poured into a flat mould to form a thin layer in the mould, and was then maintained at 80° C. for 2 days. At the end of this time the product which was stripped from the mould was a transparent sheet of rubber having a tensile strength of 1850 lb./square inch and an extension at break of 730%.

#### EXAMPLE VI.

200 parts of tetrahydrofurane were polymerised as in Example I except that 7 parts of fluorosulphonic acid were used. 65 The polyether so obtained had a molecular weight of 3,800. 100 parts of the dry polyether were heated to 150° C. with 8 parts of naphthalene 1,5 diisocyanate and mixed in a Bridge mixer for 5 minutes. At the end of this time 0.2 parts of sodium methoxide were added and mixing continued for a further 30 minutes. The product was transferred to a two roll mill, the rolls being maintained at 110° C. and 103° C. respectively, to produce a uniform crepe. 20 parts of the crepe were moulded in the form of a flat sheet in a mould heated to 150° C. under a pressure of 0.5 tons/square inch. The sheet was removed from the mould and heated at 80° C. for 16 hours. The moulded sheet so obtained was a tough abrasion resistant rubber which had a tensile strength of 2,000 lb./square inch. 85

#### EXAMPLE VII.

Tetrahydrofurane was polymerised exactly as in Example VI and 100 parts of the dry polyether were heated to 150° C. with 8 parts of naphthalene 1,5 diisocyanate for 5 minutes. 0.5 parts of tri-n-amylamine were mixed in and the mixture was poured into a flat mould to form a thin layer and then maintained at 80° C. for 2 days. The product was a tough pale brown transparent sheet of rubber which had a tensile strength of 2,100 lb./square inch. 95

#### EXAMPLE VIII.

100 parts of polytrimethylene oxide of average molecular weight 3,400 were mixed with 9 parts of naphthalene 1,5 diisocyanate in a heated Bridge mixer maintained at 150° C., for 5 minutes. 0.2 parts of barium hydroxide were added and the mixing continued for 30 minutes. The product was placed in a mould and heated to 140° C. under a pressure of 0.5 tons/square inch for a period of 20 minutes. The moulded material was removed from the mould and maintained at 80° C. for 16 hours. A tough abrasion resistant rubber was obtained. 105 110

#### EXAMPLE IX.

100 parts of polytetrahydrofurane of average molecular weight 1,600 were mixed with 14.5 parts of naphthalene 1,5 diisocyanate in a heated Bridge mixer at 130° C.—140° C. for 15 minutes. 115

0.65 parts of glycerol were then added and mixing continued for 35 minutes. The product was transferred from the mixer to a two roll mill, the rolls of which were maintained at 110° C. and 103° C. respectively, for 10 minutes. The crepe was removed from the mill and moulded into the form of a sheet in a mould heated to 140° C. and under a pressure of 0.5 tons/square inch for 15 minutes. A transparent rubber was obtained which was heat treated at 80° C. for 15 hours. The final product had a tensile strength of 2,400 lb./square inch, an extension at break of 620%, and a very low permanent set.

#### EXAMPLE X.

The process described in Example IX was repeated using 0.7 parts of 1,2,4 butane triol in place of 0.65 parts of glycerol. The final product was a strong transparent rubber.

#### EXAMPLE XI.

100 parts of polytetrahydrofuran of average molecular weight 4,000 were mixed with 8 parts of naphthalene 1,5 diisocyanate in a heated Bridge mixer at 130° C.—140° C. for 15 minutes. 0.25 parts of glycerol were then added and the mixing continued for 35 minutes. The product was transferred from the mixer to a two roll mill, the rolls of which were maintained at 110° C. and 103° C. respectively, for 10 minutes. The crepe was removed from the mill and moulded into the form of a sheet in a mould heated to 140° C. and under a pressure of 0.5 tons/square inch for 15 minutes. The sheet was removed from the mould and maintained at 80° C. for 15 hours. The final product was a tough transparent rubber.

#### EXAMPLE XII.

100 parts of polytetrahydrofuran of average molecular weight 1,600 were mixed with 16 parts of naphthalene 1,5 diisocyanate in a heated Bridge mixer at 150° C. for 30 minutes. 0.24 parts of sodium sulphate decahydrate which were equivalent to 0.13 parts of water were stirred in and stirring continued for one hour. The product was then transferred to a two roll mill, the rolls of which were heated to 110° C. and 103° C. respectively, to form a uniform crepe. The crepe was then pressed into a sheet in a mould heated to 140° C. under a pressure of 0.5 tons per square inch for 15 minutes. The sheet was removed from the mould and maintained at 80° C. for 15 hours.

A tough abrasion resistant rubber was obtained.

#### EXAMPLE XIII.

100 parts of poly-methyl trimethylene oxide of average molecular weight 8,000 were mixed with 5.25 parts of naphthalene 1,5 diisocyanate in a heated Bridge mixer at 140° C. for 15 minutes. 0.15 parts of sodium methoxide were added and the mixing continued for 30 minutes. The product was transferred to a two roll mill, the rolls of which were heated to 103° and 110° C. respectively, for 10 minutes to obtain a uniform crepe. The crepe was removed from the mill and moulded into the form of a sheet in a mould heated to 140° C. and under a pressure of 0.5 tons per square inch. The sheet was removed from the mould and maintained at 80° C. for 15 hours. The final product was a tough abrasion resistant rubber.

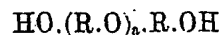
#### EXAMPLE XIV.

100 parts of polytetrahydrofuran of average molecular weight 6,000 were mixed with 6.5 parts of naphthalene diisocyanate in a heated Bridge mixer at 140° C. for 5 minutes. 0.2 parts of sodium methoxide were added, and the mixing continued for 30 minutes. The product was transferred to a two roll mill, the rolls of which were heated to 103° and 110° C. respectively, for 10 minutes to obtain a uniform crepe. The crepe was removed from the mill and moulded into the form of a sheet in a mould heated to 140° C. and under a pressure of 0.5 tons per square inch for 15 minutes. The sheet was removed from the mould and maintained at 80° C. for 15 hours.

A tough abrasion resistant rubber was obtained.

What we claim is:—

1. A process for the production of a synthetic resin which comprises reacting under substantially anhydrous conditions an excess of one or more bifunctional isocyanates with one or more linear polyethers having the formula



in which the various embodiments of R are divalent aliphatic radicals and may be the same or different, and n is an integer the average value of which is such that the average molecular weight of the polyether is greater than 1,000.

2. A process according to claim 1 in which consecutive oxygen atoms in the polyether are separated by chains of not more than four carbon atoms.

3. A process according to claim 2 in



which the polyether is polytetramethylene oxide or polytrimethylene oxide.

4. A process according to any of the preceding claims in which the bifunctional isocyanate is naphthylene 1,5 diisocyanate or hexamethylene diisocyanate, or tolylene-2,4-diisocyanate.

5. A process according to any of the preceding claims in which the polyether and bifunctional isocyanate are reacted together at an elevated temperature, preferably at between 120° C. and 160° C.

6. A process according to any of the preceding claims in which the weight of water present is not greater than 0.1% of the weight of the reaction mixture.

7. A process according to any of the preceding claims in which the polyether is free from acid.

8. A process according to claim 7, in which the polyether is rendered free from acid by the addition of a basic substance.

9. A process according to claim 8, in which the basic substance is a tertiary organic base.

10. A process according to claim 9 in which the basic substance is trimethyl-

amine.

11. A process according to any of the preceding claims in which the average molecular weight of the polyether is greater than 1,400.

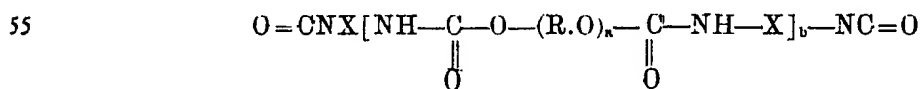
12. A process according to any of the preceding claims in which the average molecular weight of the polyether is less than 5,000 and the amount of bifunctional isocyanate is less than 2 moles per moles of polyether.

13. A process according to any of claims 1 to 11, in which the polyether has an average molecular weight not less than 5,000, preferably not less than 7,000, and in which the amount of bifunctional isocyanate is not less than 2 moles per mole of polyether.

14. A process according to claim 13 in which the amount of bifunctional isocyanate is from 2 to 2.6 moles per mole of polyether.

15. A synthetic resin produced according to any of the processes of the preceding claims.

16. A synthetic resin represented by the formula:—



in which the various embodiments of R are divalent aliphatic hydrocarbon radicals and may be the same or different, the various embodiments of x are divalent organic radicals and may be the same or different, a and b are integers and the average value of a is such that the average molecular weight of HO(RO)<sub>a</sub>H is greater than 1,000.

17. A synthetic resin according to claim 16 in which R is —



18. A synthetic resin according to claim 16 in which R is



19. A synthetic resin according to any of claims 16 to 18 in which the average value of a is such that the average molecular weight of HO(RO)<sub>a</sub>H is greater than 1400.

20. A synthetic resin according to any of claims 16 to 19 in which the average value of b is such that the synthetic resin has an average molecular weight of at least 2000.

21. A synthetic resin according to any of claims 16 to 20 in which the average value of a is such that the average mole-

cular weight of HO(RO)<sub>a</sub>H is less than 5000 and the value of b in the majority of the molecules is 2 or more.

22. A synthetic resin according to any of claims 16 to 20 in which the average value of a is such that the average molecular weight of HO(RO)<sub>a</sub>H is greater than 5000, preferably greater than 7,000, and the value of b in the majority of the molecules is one.

23. A synthetic resin according to any of claims 16 to 22 in which some or all of the embodiments of X are divalent aromatic radicals.

24. A synthetic resin according to claim 23 in which some or all of the embodiments of X are phenylene radicals.

25. A synthetic resin according to claim 23 in which some or all of the embodiments of X are tolylene radicals.

26. A synthetic resin according to claim 23 in which some or all of the embodiments of X are naphthylene radicals.

27. A synthetic resin according to any of claims 16 to 22 in which some or all of the embodiments of X are divalent aliphatic radicals.

28. A synthetic resin according to claim 27 in which some or all of the embodiments of X are alkylene radicals.

29. A synthetic resin according to

claim 28 in which some or all of the embodiments of X are



radicals.

- 5 30. A modification of a synthetic resin according to any of claims 15 to 29 in which some of the resin chains are chemically linked together but in which this linking is so limited that the resin is still capable of being moulded.

- 10 31. The production of a rubber like material by a process which comprises heating a synthetic resin according to any of claims 15 to 30 in the presence of a basic catalyst.

- 15 32. A process according to claim 31 wherein the catalyst is an inorganic basic compound.

- 20 33. A process according to claim 31 wherein the catalyst is an organic tertiary base.

34. A process according to claim 31 wherein the catalyst is an alkoxide.

- 25 35. A process according to any of claims 31 to 34 in which the weight of catalyst used is from 0.05 to 0.5% of the weight of the synthetic resin.

- 30 36. The modification of a synthetic resin according to any of claims 15 to 30 by reacting said resin with water, steam, or ammonia, the reaction being continued, if desired, until a rubber-like material is produced, the water if desired being in the form of a hydrated salt.

- 35 37. The modification of a synthetic resin according to any of claims 15 to 30 by reacting said resin with at least one compound having two groups reactable with the isocyanate group, the reaction being continued, if desired, until a rubber-like material is produced.

- 40 38. A process according to claim 37 in which said compound is a glycol.

- 45 39. A process according to claim 37 in which said compound is a diamine.

- 50 40. A process according to any of claims 36 to 39 in which said compound or the water, steam or ammonia is present to an extent sufficient to bring about polyaddition between only a proportion of the isocyanate groups.

- 55 41. A process according to any of claims 36 to 40, in which the synthetic resin is reacted with said compound, water, steam or ammonia, at a temperature from 120 to 160° C.

42. Modified synthetic resins whenever prepared by a process claimed in any of claims 36 to 41.

- 60 43. Modified synthetic resins whenever prepared by processes described herein.

44. The production of a rubber-like material by a process which comprises

subjecting to heat or catalytic action a modified synthetic resin according to any of claims 42, 43, 59 and 60.

45. A composition comprising a synthetic resin according to any of claims 15 to 30 and a polyhydroxy compound containing at least three hydroxyl groups.

46. A composition according to claim 45 in which the proportions of the synthetic resin and the polyhydroxy compound are such that the hydroxyl groups and terminal isocyanate groups are present in substantially equivalent amounts, with if desired, a slight excess of isocyanate groups over hydroxyl groups.

47. The production of a rubber-like material by a process which comprises subjecting to heat or catalytic action a composition according to any of claims 45, 46 and 63.

48. A process for the production of a rubber-like material according to any of claims 31 to 35 or claim 44 or claim 47, which comprises pouring the synthetic resin, modified synthetic resin or composition in the fluid state into an open mould and subjecting it to an elevated temperature under atmospheric pressure.

49. A process for the production of a rubber-like material and according to any of claims 31 to 35 or claim 44 or claim 47, which comprises introducing the synthetic resin, modified synthetic resin or composition into a mould and subjecting it to an elevated temperature when under the influence of pressure.

50. Rubber-like materials when prepared by a process claimed in either of claims 48 and 49.

51. Synthetic resins whenever prepared by processes described herein.

52. Rubber-like materials whenever prepared by processes described herein.

53. Rubber-like materials comprising polyether chains chemically linked together by residues of at least one bifunctional isocyanate and/or derivatives thereof, wherein the polyether chains each have the formula  $-\text{R}(\text{O.R.})_n-$  in which the various embodiments of R are divalent aliphatic hydrocarbon radicals and may be the same or different, and n is an integer the average value of which is such that the average molecular weight of  $\text{HO.R}(\text{O.R.})_n\text{OH}$  is at least 1,000.

54. Rubber-like materials according to claim 53 wherein the polyether chains are polytrimethylene oxide chains.

55. Rubber-like materials according to claim 53 wherein the polyether chains are polytetramethylene oxide chains.

56. Shaped articles comprising rubber-like materials claimed in any of claims 53 to 55.

57. Shaped articles produced by the process of either of claims 48 and 49.

58. Shaped articles whenever produced by a process described hereinbefore.
59. Modified synthetic resins substantially as described in Examples I, III(b) and XII.
60. A modified synthetic resin substantially as described in Example II.
61. Synthetic resins substantially as described in the Examples I to XII.
62. Synthetic resins substantially as described in Examples XIII and XIV.
63. A composition comprising a synthetic resin and a polyhydroxy compound substantially as described herein.
64. Compositions comprising a synthetic resin and a polyhydroxy compound substantially as described in Examples IX, X and XI.
65. Rubber-like materials substantially as described in Examples I, III(b) and XII.
66. A rubber-like material substantially as described in Example II.
67. Rubber-like materials substantially as described in Examples IIIa, and IV to VIII.
68. Rubber-like materials substantially as described in Examples IX, X, XI, XIII and XIV.
69. Rubber-like materials when prepared by a process claimed in any of claims 31 to 35.
70. Rubber-like materials when prepared by a process claimed in claim 44.
71. Rubber-like materials when prepared by a process claimed in claim 47.
- WALTER SCOTT,  
Agent for the Applicants.

# PROVISIONAL SPECIFICATION

No. 9207 A.D. 1952

## New Synthetic Resins Derived from Linear Aliphatic Polyethers and Bifunctional Isocyanates and Rubber-Like Materials derived therefrom

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare this invention to be described in the following statement:—

This invention relates to new synthetic resins which can be converted into rubber-like materials and to rubber-like materials produced therefrom.

By the term rubber-like as used throughout this specification we mean having physical properties similar to those of vulcanised natural rubber.

According to the present invention we provide a linear synthetic resin having polyether chains linked by urethane groups and having terminal isocyanate groups, by a process which comprises cyanates with one or more linear polyethers having terminal hydroxyl groups under substantially anhydrous conditions and thereafter subjecting the product of the reaction to treatment with water or steam. We have found that a rubber-like material having an outstanding combination of resistance to abrasion, resistance to hydrolytic degradation and resistance to swelling by aliphatic and aromatic hydrocarbons may be produced by subjecting this linear synthetic resin to an elevated temperature.

Suitable diisocyanates which may be used are for example, hexamethylene diisocyanate; 2 - nitrodiphenylene - 4, 4'-diisocyanate; 2 - nitrodiphenylmethane-

4,4' - diisocyanate; naphthylene - 1,4-diisocyanate; naphthylene - 1 - 5 - diisocyanate; naphthylene - 2,7-diisocyanate; fluorene - diisocyanate; chrysene-diisocyanate; 1 - chlorophenylene-2,4-diisocyanate; tolylene-2,4-diisocyanate; dicyclohexylmethane - 4,4' - diisocyanate, di - para-xylylmethane-4,4'-diisocyanate; diphenylene-4,4'-diisocyanate and 4,4'-cyclohexylphenyl diisocyanate. Suitable mixtures of any of these compounds may be used.

The polyether reagents may contain a minor proportion of other linear compounds having terminal groups which are reactable with diisocyanates, such as for example glycols.

Suitable linear polyethers include for example, those prepared by the polymerisation or co-polymerisation of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofurane, dioxanes, and dioxolanes; polycondensation products of glycols; and derivatives of any of these compounds. Such polyethers may be prepared by any suitable known method, for example, ethylene oxide may be polymerised by the action of water, glycol, acetic anhydride or caustic soda. Tetrahydrofurane may be polymerised by the action of catalytic amounts of fluoro-sulphonic acid, or boron trifluoride and ethylene oxide or propylene oxide, followed by treatment with water.

The preferred average molecular weight range for the polyether is 1,400 to

15,000 and especially the range 1,400 to 5,000.

Depending upon the method of preparation, the polyether may have terminal groups which are not reactable with the diisocyanates. In such circumstances the non-reactable terminal group may be replaced by the reactable hydroxyl groups by known methods.

In carrying out the process of our invention the polyether is reacted with the diisocyanate preferably at an elevated temperature such as for example 100—140° C. This enables the reaction to be completed rapidly, usually within a matter of a few minutes. The reaction must be carried out under substantially anhydrous conditions, that is to say, water must be excluded to a sufficient extent that the reaction proceeds mainly between the polyether hydroxyl groups and the isocyanate groups. We have found that the reaction proceeds satisfactorily provided the water content of the reaction mixture does not exceed about 0.02%. The polyether is most conveniently dried before carrying out the reaction by melting in a current of a dry inert gas, e.g. nitrogen or carbon dioxide, preferably at an elevated temperature, e.g. 120° C. and if desired under reduced pressure.

A sufficient excess of diisocyanate or mixture of these should be used to ensure that the reaction product has terminal isocyanate groups. The ratio of our reagents and their molecular weights and their structures also control the rheological properties of our products. The amount of diisocyanate or mixture of these required will depend upon these factors and particularly useful amounts of diisocyanate or mixtures of these are 1.2 to 2 moles per mole of polyether.

The product of this reaction is then treated with water or steam by passing steam into or on to the surface of the product or by adding the required amount of water. The amount of steam or water used is the amount which results

in the required plastic flow or viscosity in the product. For this only an amount sufficient to bring about condensation between a proportion of terminal isocyanate groups is required. Excess steam or water should be avoided because it is difficult to remove without destroying the thermoplastic properties of our product. The amount of steaming or of water treatment is, in fact, often best judged by observing the change in a rheological property of the reaction product. Amounts of water used are normally between 0.4 and 1.5% by weight of the material being treated.

An important feature in controlling the rheological properties of our product is the control of the uniformity of the steaming or water treatment reaction step. Normal means of mixing and temperature control may be used for this purpose.

The reaction product is conveniently converted into the form of chips, ribbon, film, sheets, fibres, filaments, solutions or dispersions, the chips being particularly suitable for moulding into articles, and solutions and dispersions for coatings and impregnation.

The linear synthetic resin of our invention may be converted into a rubber-like material by heating to an elevated temperature of, for example, 150—170° C. for a period of, for example 10—15 minutes. The formation of the rubber-like material may be speeded up by incorporating into the linear synthetic resin a suitable catalyst such as for example an organic basic compound, e.g. pyridine.

At any stage before the final heating step, ancillary ingredients such as for example, fillers, plasticisers, extenders, pigments or other materials, may be incorporated in the material in order to affect the properties of the rubber-like material in some desired manner.

WALTER SCOTT,  
Agent for the Applicants.

# PROVISIONAL SPECIFICATION

No. 9208 A.D. 1952

## New Synthetic Resins Derived from Linear Aliphatic Polyethers and Bifunctional Isocyanates and Rubber-Like Materials derived therefrom

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare this invention

to be described in the following statement:—

This invention relates to new synthetic resins which can be converted into

rubber-like materials and to rubber-like materials produced therefrom.

By the term rubber-like as used throughout this specification we mean having physical properties similar to those of vulcanised natural rubber.

According to the present invention we provide a linear synthetic resin having polyether chains linked by urethane groups and having terminal isocyanate groups, by a process which comprises reacting an excess of one or more diisocyanates with one or more linear polyethers having terminal hydroxyl groups under substantially anhydrous conditions and thereafter subjecting the product of the reaction to treatment with a glycol. We have found that a rubber-like material having an outstanding combination of resistance to abrasion, resistance to hydrolytic degradation and resistance to swelling by aliphatic and aromatic hydrocarbons may be produced by subjecting this linear synthetic resin to an elevated temperature.

Suitable diisocyanates which may be used are for example, hexamethylene diisocyanate; 2-nitrodiphenylene-4,4'-diisocyanate; 2-nitrodiphenylmethane-4,4'-diisocyanate; naphthylene-1,4-diisocyanate; naphthylene-1,5-diisocyanate; naphthylene-2,7-diisocyanate; fluorene-diisocyanate; chrysene-diisocyanate; 1-chlorophenylene-2,4-diisocyanate; tolylene-2,4-diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; di-para-xylylmethane-4,4'-diisocyanate; diphenylene-4,4'-diisocyanate and 4,4'-cyclohexylphenyl diisocyanate. Suitable mixtures of any of these compounds may be used.

The polyether reagents may contain a minor proportion of other linear compounds having such terminal groups which are reactable with diisocyanates, such as for example glycols.

Suitable linear polyethers include for example, those prepared by the polymerisation or co-polymerisation of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofurane, dioxanes, and dioxolanes; poly-condensation products of glycols; polyether acetals; and derivatives of any of these compounds. Such polyethers may be prepared by any suitable known method, for example, ethylene oxide may be polymerised by the action of water, glycol, acetic anhydride or caustic soda. Tetrahydrofurane may be polymerised by the action of catalytic amounts of fluorosulphonic acid, or boron trifluoride and ethylene oxide or propylene oxide, followed by treatment with water.

The preferred average molecular

weight range for the polyether, polythioether or polyether-thioether is 1,400 to 15,000 and especially the range 1,400 to 5,000.

Depending upon the method of preparation, the polyether may have terminal groups which are not reactable with the diisocyanates. In such circumstances the non-reactable terminal group may be replaced by hydroxyl groups by known methods.

In carrying out the process of our invention the polyether is reacted with the diisocyanate preferably at an elevated temperature such as for example 100—140° C. This enables the reaction to be completed rapidly, usually within a matter of a few minutes. The reaction must be carried out under substantially anhydrous conditions, that is to say, water must be excluded to a sufficient extent that the reaction proceeds mainly between the polyether terminal groups and the isocyanate groups. We have found that the reaction proceeds satisfactorily provided the water content of the reaction mixture does not exceed about 0.02%. The polyether is most conveniently dried before carrying out the reaction by melting in a current of a dry inert gas, e.g. nitrogen or carbon dioxide, preferably at an elevated temperature, e.g. 120° C. and if desired under reduced pressure.

A sufficient excess of diisocyanate or mixture of these should be used to ensure that the reaction product has terminal isocyanate groups. The ratio of our reagents and their molecular weights and their structures also control the rheological properties of our products. The amount of diisocyanate or mixture of these required will depend upon these factors and particularly useful amounts of diisocyanate or mixtures of these are 1.2 to 2 moles per mole of polyether.

The product of this reaction is then treated with a glycol. The amount of glycol used is the amount which results in the required plastic flow or viscosity in the product. For this, only an amount sufficient to bring about poly-addition between a proportion of terminal isocyanate groups and the hydroxyl groups is required. Excess glycol should be avoided because it is difficult to remove without destroying the thermoplastic properties of our product.

An important feature in controlling the rheological properties of our product is the control of the uniformity of the reaction. Normal means of mixing and temperature control may be used for this purpose.

The reaction product is conveniently

converted into the form of chips, ribbon, film, sheets, fibres, filaments, solutions or dispersions, the chips being particularly suitable for moulding into articles, and solutions and dispersions for coatings and impregnation.

The linear synthetic resin of our invention may be converted into a rubber-like material by heating to an elevated temperature of, for example, 150—170° C. The formation of the rubber-like material may be speeded up by incorporating into the linear synthetic resin

a suitable catalyst such as for example an organic basic compound, e.g. pyridine.

At any stage before the final heating step, ancillary ingredients such as for example, fillers, plasticisers, extenders, pigments or other materials, may be incorporated in the material in order to affect the properties of the rubber-like material in some desired manner.

WALTER SCOTT,  
Agent for the Applicants.

# PROVISIONAL SPECIFICATION

No. 16214 A.D. 1952

## New Synthetic Resins Derived from Linear Aliphatic Polyethers and Bifunctional Isocyanates and Rubber-Like Materials derived therefrom

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare this invention to be described in the following statement:—

This invention relates to new synthetic resins which can be converted into rubber-like materials and to rubber-like materials produced therefrom.

By the term rubber-like as used throughout this specification we mean having physical properties similar to those of vulcanised natural rubber.

According to the present invention we provide a linear synthetic resin having polyether chains linked by urethane groups and having terminal isocyanate groups, by a process which comprises reacting an excess of one or more diisocyanates with one or more linear polyethers having terminal hydroxyl groups under substantially anhydrous conditions and thereafter subjecting the product of the reaction to treatment with one or more compounds each having two groups each reactable with isocyanate groups. We have found that a rubber-like material having an outstanding combination of resistance to abrasion, resistance to hydrolytic degradation and resistance to swelling by aliphatic and aromatic hydrocarbons may be produced by subjecting this linear synthetic resin to an elevated temperature.

The polyether reagents may contain a minor proportion of other linear compounds having terminal groups reactable with diisocyanates, such as for example glycols.

Suitable diisocyanates which may be used are for example, hexamethylene di-

isocyanate; 2-nitrodiphenylene-4,4'-diisocyanate; 2-nitrodiphenylmethane-4,4'-diisocyanate; naphthylene-1,4-diisocyanate; naphthylene-1,5-diisocyanate; naphthylene-2,7-diisocyanate; fluorene-diisocyanate; chrysene-diisocyanate; 1-chlorophenylene-2,4-diisocyanate; tolylene-2,4-diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; di-para-xylylmethane-4,4'-diisocyanate; diphenylene-4,4'-diisocyanate and 4,4'-cyclohexylphenyl diisocyanate. Suitable mixtures of any of these compounds may be used.

Suitable linear polyethers include for example, those prepared by the polymerisation or co-polymerisation of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, dioxanes, and dioxolanes; poly-condensation products of glycols; and derivatives of any of these compounds. Such polyethers may be prepared by any suitable known method, for example, ethylene oxide may be polymerised by the action of water, glycol, acetic anhydride or caustic soda. Tetrahydrofuran may be polymerised by the action of catalytic amounts of fluorosulphonic acid, or boron trifluoride and ethylene oxide or propylene oxide, followed by treatment with water.

The preferred average molecular weight range for the polyether is 1,400 to 15,000 and especially the range 1,400 to 5,000.

Depending upon the method of preparation, the polyether may have terminal groups which are not reactable with the diisocyanates or diisothiocyanates. In such circumstances the non-reactable terminal group may be replaced by hydroxyl groups by known methods.



The compound or compounds each having two groups each reactable with isocyanate or isothiocyanate groups include for example diamines having primary or secondary amino groups, dicarboxylic acids, diamides and amino acids.

In carrying out the process of our invention the polyether is reacted with the diisocyanate preferably at an elevated temperature such as for example 100—140° C. This enables the reaction to be completed rapidly, usually within a matter of a few minutes. The reaction must be carried out under substantially anhydrous conditions, that is to say, water must be excluded to a sufficient extent that the reaction proceeds mainly between the polyether terminal groups and the isocyanate groups. We have found that the reaction proceeds satisfactorily provided the water content of the reaction mixture does not exceed about 0.02%. The polyether is most conveniently dried before carrying out the reaction by melting in a current of a dry inert gas, e.g. nitrogen or carbon dioxide, preferably at an elevated temperature, e.g. 120° C. and if desired under reduced pressure.

A sufficient excess of diisocyanate or mixture of these should be used to ensure that the reaction product has terminal isocyanate groups. The ratio of our reagents and their molecular weights and their structures also control the rheological properties of our products. The amount of diisocyanate or mixture of these required will depend upon these factors and particularly useful amounts of diisocyanate or mixtures of these are 1.2 to 2 moles per mole of polyether.

The product of this reaction is then treated with a compound or compounds each having two groups each reactable with isocyanate groups as hereinbefore

described. The amount of any one or more of these compounds used is the amount which results in the required plastic flow or viscosity in the product. For this only an amount sufficient to bring about poly-addition between a proportion of terminal isocyanate groups and the groups reactable therewith in said compounds is required. Excess of said compounds should be avoided because it is difficult to remove the excess without destroying the thermoplastic properties of our product.

An important feature in controlling the rheological properties of our product is the control of the uniformity of the reaction. Normal means of mixing and temperature control may be used for this purpose.

The reaction product is conveniently converted into the form of chips, ribbon, film, sheets, fibres, filaments, solutions or dispersions, the chips being particularly suitable for moulding into articles, and solutions and dispersions for coatings and impregnation.

The linear synthetic resin of our invention may be converted into a rubber-like material by heating to an elevated temperature of, for example, 150—170° C. The formation of the rubber-like material may be speeded up by incorporating into the linear synthetic resin a suitable catalyst such as for example an organic basic compound, e.g. pyridine.

At any stage before the final heating step, ancillary ingredients such as for example, fillers, plasticisers, extenders, pigments or other materials, may be incorporated in the material in order to affect the properties of the rubber-like material in some desired manner.

WALTER SCOTT,  
Agent for the Applicants.

#### PROVISIONAL SPECIFICATION

No. 28605 A.D. 1952

### New Synthetic Resins Derived from Linear Aliphatic Polyethers and Bifunctional Isocyanates and Rubber-Like Materials derived therefrom

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare this invention to be described in the following statement:—

This invention relates to new plastic compositions which can be converted into rubber-like materials and to rubber-like materials produced therefrom.

By the term rubber-like as used throughout this specification we mean having physical properties similar to those of vulcanised natural rubber.

According to the present invention we provide a composition obtained by mixing a linear synthetic resin comprising polyether chains having terminal isocyanate groups with a compound having at least three hydroxyl groups, the linear

synthetic resin being produced by reacting under substantially anhydrous conditions an excess of one or more diisocyanates with one or more linear polyethers having terminal groups reactable therewith. We have found that a rubber-like material having an outstanding combination of high tensile strength, high tear resistance, resistance to abrasion, resistance to hydrolytic degradation and resistance to swelling by aliphatic and aromatic hydrocarbons may be produced by subjecting the composition of our invention to an elevated temperature.

Suitable diisocyanates which may be used are for example, hexamethylene diisocyanate; 2-nitrodiphenylene-4,4'-diisocyanate; 2-nitrodiphenylmethane-4,4'-diisocyanate; naphthylene-1,4-diisocyanate; naphthylene-1,5-diisocyanate; naphthylene-2,7-diisocyanate; fluorene-diisocyanate; chrysene-diisocyanate; 1-chlorophenylene-2,4-diisocyanate; tolylene-2,4-diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; di-para-xylylmethane-4,4'-diisocyanate; diphenylene-4,4'-diisocyanate and 4,4'-cyclohexylphenyl diisocyanate. Mixtures of any of these compounds may be used.

Compositions having at least three hydroxyl groups may be polyfunctional aliphatic alcohols having primary and/or secondary hydroxyl groups. Mixtures of these compounds may be used. Examples of suitable polyhydroxy compounds are glycerol, pentaerythritol, trihydroxy tertiary butane, trimethylol propane, trimethylol ethane, and 1:2:4 butane triol.

Suitable linear polyethers include, for example, those prepared by the polymerisation or co-polymerisation of ethylene oxide, isopropylene oxide, trimethylene oxide, tetrahydrofuran, dioxanes, and dioxolanes; polycondensation products of glycols; polyether acetals; and derivatives of any of these compounds. Such polyethers may be prepared by any suitable known methods, for example, ethylene oxide may be polymerised by the action of water, glycol, acetic anhydride or caustic soda. Tetrahydrofuran may be polymerised by the action of catalytic amounts of fluorosulphonic acid or boron trifluoride and ethylene oxide or propylene oxide, followed by treatment with water.

Depending upon the method of preparation the polyether may have terminal groups which are not reactable with diisocyanates, and in such circumstances the non-reactable terminal groups should be replaced by hydroxyl groups by known methods.

In preparing the linear synthetic resin the polyether is reacted with the diiso-

cyanate preferably at an elevated temperature, for example 120°—160° C. This enables the reaction to be completed rapidly. The reaction must be carried out under substantially anhydrous conditions, that is to say, water must be excluded to a sufficient extent that the reaction proceeds essentially between the polyether terminal groups and the isocyanate groups. We have found that the reaction proceeds satisfactorily provided the water content of the reaction mixture does not exceed about 0.02% of the weight of the reaction mixture. The polyether is most conveniently dried before carrying out the reaction by heating in the liquid state in a current of a dry inert gas, e.g. nitrogen or carbon dioxide, e.g. at 120° C., and if desired, under reduced pressure.

It is necessary that an excess of diisocyanate over the polyether should be used in order to produce a synthetic linear resin having terminal isocyanate groups. The relative amount of diisocyanate will determine to what extent chain lengthening of the polyether molecules is allowed to proceed. Thus, when the amount of diisocyanate is only slightly more than one mole per mole of polyether, there will be a considerable degree of chain lengthening. When the amount of diisocyanate is greater than two moles per mole of polyether there will be substantially no chain lengthening of the polyether. The rheological properties of the linear synthetic resin are controlled by the ratio of the reactants, by their molecular weights and their structures. It is necessary therefore to vary the amount of diisocyanate which is used according to the molecular weight of the polyether.

With polyethers having a molecular weight below 5,000 it is desirable that there should be some chain lengthening during the initial treatment with the diisocyanate, and for such polyethers particularly useful amounts of diisocyanate are from 1.2 to 2 moles per mole of polyether. With polyethers having a molecular weight above 5,000 and particularly those above 10,000, we prefer that there should be no substantial degree of chain lengthening. Although theoretically this can be achieved by using 2 moles of diisocyanate per mole of polyether, we prefer to use an excess of from 5% to 10% over the theoretical amount of diisocyanate.

The compositions of our invention are prepared by mixing the required amount of the polyhydroxy compound into the linear synthetic resin until a homogeneous product is obtained. For ease of working

it is usually found convenient to mix the polyhydroxy compound into the hot linear synthetic resin immediately after it has been prepared. Where, however, it is not intended to convert our composition into a rubber-like material immediately after its preparation it should be cooled to room temperature or below. The relative amounts of the polyhydroxy compound and the linear synthetic resin should be such that the hydroxyl groups and terminal isocyanate groups are present in substantially equivalent amounts. The amount of polyhydroxy compound required for this purpose will therefore depend upon the molecular weight of the linear synthetic resin.

The composition of our invention is preferably used for moulding purposes within a comparatively short time of its preparation. The reaction between the polyhydroxy compound and the linear synthetic resin can be retarded to a certain extent by cooling to a low temperature, but the composition should

preferably be kept not more than a few hours before being subjected to the moulding operation.

The composition is conveniently converted into the form of chips, ribbon, film, sheets, fibres, filaments, solutions or dispersions, the chips being particularly suitable for moulding into articles, and solutions and dispersions for coatings and impregnation.

The composition of our invention may be converted into a rubber-like material by heating to an elevated temperature of, for example, 150—170° C. for a period of, for example, 10—30 minutes. In some cases it may be desirable in addition, to subject the composition to pressure of the order of 1 ton per square inch.

At any stage before the final heating step, ancillary ingredients such as, for example, fillers, plasticisers, extenders, pigments or other materials, may be incorporated in the material.

WALTER SCOTT,

Agent for the Applicants.

# PROVISIONAL SPECIFICATION

No. 28606 A.D. 1952

## New Synthetic Resins Derived from Linear Aliphatic Polyethers and Bifunctional Isocyanates and Rubber-Like Materials derived therefrom

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare this invention to be described in the following statement:—

This invention relates to new synthetic resins which can be converted into rubber-like materials and to rubber-like materials produced therefrom.

By the term rubber-like as used throughout this specification we mean having physical properties similar to those of vulcanised natural rubber.

According to the present invention we provide a linear synthetic resin comprising polyether chains having terminal isocyanate groups by a process which comprises reacting under substantially anhydrous conditions an excess of one or more diisocyanates with one or more linear polyethers having terminal hydroxyl groups. We have found that a rubber-like material having an outstanding combination of high tensile strength, high tear resistance, resistance to abrasion, resistance to hydrolytic degradation and resistance to swelling by aliphatic and aromatic hydrocarbons may be pro-

duced by first reacting the linear synthetic resin of our invention with water, steam, ammonia or a compound having two groups each reactable with the isocyanate group, and thereafter subjecting the reaction product to an elevated temperature.

Suitable diisocyanates which may be used are for example, hexamethylene diisocyanate; 2-nitrodiphenylene-4,4'-diisocyanate; 2-nitrodiphenylmethane-4,4'-diisocyanate; naphthylene-1,4-diisocyanate; naphthalene-1-5-diisocyanate; naphthylene-2,7-diisocyanate; fluorene-diisocyanate; chrysene-diisocyanate; 1-chlorophenylene-2,4-diisocyanate; tolylene-4,4'-diisocyanate; dicyclohexylmethane-4,4'-diisocyanate; di-para-xylylmethane-4,4'-diisocyanate; diphenylene-4,4'-diisocyanate and 4,4'-cyclohexylphenyl diisocyanate. Mixtures of any of these compounds may be used.

Suitable linear polyethers include, for example, those prepared by the polymerisation or co-polymerisation of ethylene oxide, isopropylene oxide, trimethylene oxide, tetrahydrofurane, dioxanes, and dioxolanes; polycondensation products of glycols; polyether acetals; and

derivatives of any of these compounds. Such polyethers may be prepared by any suitable known method, for example, ethylene oxide may be polymerised by the action of water, glycol, acetic anhydride or caustic soda. Tetrahydrofuran may be polymerised by the action of catalytic amounts of fluorosulphonic acid or boron trifluoride and ethylene oxide or propylene oxide, followed by treatment with water.

Depending upon the method of preparation, the polyether may have terminal groups which are not reactable with diisocyanates, and in such circumstances the non-reactable terminal groups may be replaced by hydroxyl groups by known methods.

Compounds having two groups each reactable with the isocyanate group and which may be reacted with the linear synthetic resin of our invention, include glycols, diamines having primary or secondary amino groups, dicarboxylic acids, hydroxy amines, hydroxy acids and amino acids. Suitable compounds are, for example, ethylene glycol, 1:3 propane diol, 1:4 butane diol, ethylene diamine, trimethylene diamine, tetramethylene diamine, *m*-phenylene diamine, naphthylene diamines, tolylene 2,4 diamine, aminobenzyl aniline, aminodiphenylamine, 2-amino ethyl alcohol, 2-amino 1 naphthol, *m*-aminophenol, glycollic acid,  $\alpha$ -hydroxy-propionic acid, amino acetic acid and amino benzoic acid.

In carrying out the process of our invention the polyether is reacted with the diisocyanate preferably at an elevated temperature, for example 120°—160° C. This enables the reaction to be completed rapidly. The reaction must be carried out under substantially anhydrous conditions, that is to say, water must be excluded to a sufficient extent that the reaction proceeds essentially between the polyether terminal groups and the isocyanate groups. We have found that the reaction proceeds satisfactorily provided the water content of the reaction mixture does not exceed about 0.02% of the weight of the reaction mixture. The polyether is most conveniently dried before carrying out the reaction by heating e.g. at 120° C. in the liquid state in a current of a dry inert gas, e.g. nitrogen or carbon dioxide, and, if desired, under reduced pressure.

It is necessary that an excess of diisocyanate over the polyether should be used in order to produce a synthetic linear resin having terminal isocyanate groups. The relative amount of diisocyanate will determine to what extent chain lengthen-

ing of the polyether molecules is allowed to proceed. Thus, when the amount of diisocyanate is only slightly more than one mole per mole of polyether, there will be a considerable degree of chain lengthening. When the amount of diisocyanate is greater than two moles per mole of polyether there will be substantially no chain lengthening of the polyether. The rheological properties of our product are controlled by the ratio of the reactants, by their molecular weights and their structures. It is necessary therefore to vary the amount of diisocyanate which is used according to the molecular weight of the polyether.

With polyethers having a molecular weight below 5,000 it is desirable that there should be some chain lengthening during the treatment with the diisocyanate, and for such polyethers particularly useful amounts of diisocyanate are from 1.2 to 2 moles per mole of polyether. With polyethers having a molecular weight above 5,000 and particularly those above 10,000, we prefer that there should be no substantial degree of chain lengthening. Although theoretically this can be achieved by using 2 moles of diisocyanate per mole of polyether, we prefer to use an excess of from 5% to 10% over the theoretical amount of diisocyanate.

The linear synthetic resins of our invention may then be reacted with a suitable compound of the kind hereinbefore described, to obtain a product which after a suitable heat treatment yields a rubber-like material. The reactant, e.g. water, may be added in the required amount to the synthetic linear resin in a suitable mixing vessel, or, in the case of steam and ammonia it may be blown on to the surface of the product. The rheological properties of the rubber-like product which may be obtained depends upon the nature of the synthetic resin of our invention and the nature and particularly the amount of the reactant with which it is reacted. For this only an amount of reactant sufficient to bring about poly-addition between a proportion of the terminal isocyanate groups is required. The amount of reactant used is, in fact, best judged by observing the change in a rheological property of the rubber-like product. When the reactant to be used is not volatile at the reaction conditions, and the amount required has been determined by trial, it may then be added to the synthetic resin of our invention in weighed amount. When losses of the reactant occur, e.g. because of volatility in the case of steam, special process control to ensure correct addition is

required. Interaction between the reactant molecules, e.g. in the case of glycols, may also make special process control necessary. When water is used the amount is normally between 0.4 and 1.5% by weight of the material being treated. Excess of the reactant should be avoided because it has a degrading effect on the physical properties of our final cured rubber-like material.

An important feature in controlling the rheological properties of our product is the control of the uniformity of the reaction between the linear synthetic resins of our invention and the compounds of the kind hereinbefore described. Where the reaction product is sufficiently fluid the reaction may be carried out solely in a stirred mixer. In other cases the initial stage of the reaction may be carried out in a stirred mixer but as the reaction proceeds the nature of the product changes and in order to keep the product effectively mixed so that the reaction can proceed to the desired extent, the final stage of the mixing should preferably be carried out on heated rolls or in a mixer of the Banbury type. The temperature at which this reaction is allowed to proceed will depend upon the type of compound with which the synthetic linear resin of our reaction is reacted. When water is used the reaction can be carried out below 100° C., e.g., at 80° C., but we prefer to use higher temperatures of the order of 120—160° C. and when the material is further reacted under masticating conditions we prefer this further reaction to be at 110—140° C. The reaction with steam is similarly preferably carried out at temperatures from 120—160° C. followed, if desired, by mastication at, for example, 110—140° C. With diamines, dicarboxylic acids and amino acids, on the other hand, it is preferred

that the synthetic linear resin should be cooled before the reaction is allowed to begin in order to allow thorough mixing of the ingredients before further reaction at the higher temperatures.

The reaction product is conveniently converted into the form of chips, ribbon, film, sheets, fibres, filaments, solutions or dispersions, the chips being particularly suitable for moulding into articles, and solutions and dispersions for coatings and impregnation.

The reaction product may thereafter be converted into a rubber-like material by heating to an elevated temperature of, for example, 150—170° C. for a period of, for example, 10—30 minutes if necessary at a pressure of the order of 1 ton/square inch. Where the reaction product is sufficiently fluid, the product may be poured into an open mould and converted into a rubber-like material by heating without the application of pressure. Also where such a fluid reaction product has been prepared from a reactant, e.g. water or steam, which gives rise to the evolution of a gas during the reaction, an expanded rubber-like material may be obtained by heating the reaction product in a suitable mould. The formation of the rubber-like material may be speeded up or carried out at a lower temperature by incorporating into the linear synthetic resin a suitable catalyst. When the linear synthetic resin has been reacted with water, steam or a dicarboxylic acid, a suitable catalyst is an organic basic compound, e.g. pyridine.

At any stage before the final heating step, ancillary ingredients such as, for example, fillers, plasticisers, extenders, pigments, or other materials, may be incorporated in the material.

WALTER SCOTT,  
Agent for the Applicants.